

## LETTERS

# Changing boreal methane sources and constant biomass burning during the last termination

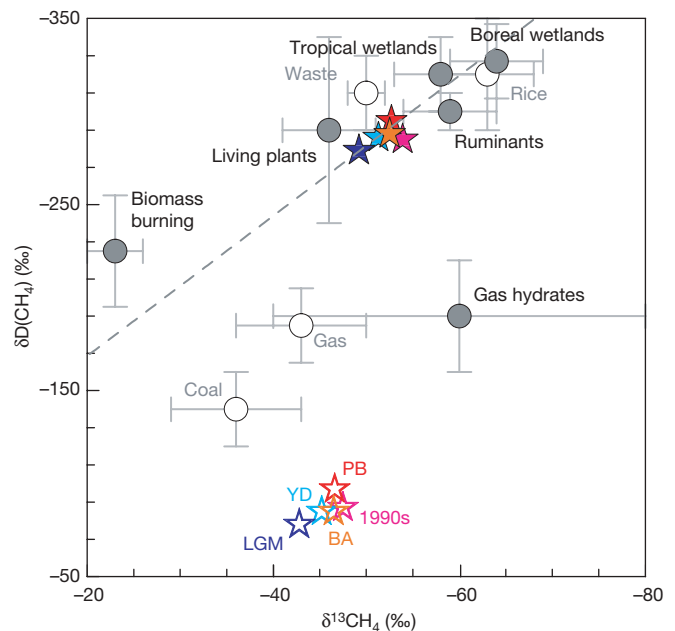
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Past atmospheric methane concentrations show strong fluctuations in parallel to rapid glacial climate changes in the Northern Hemisphere<sup>1,2</sup> superimposed on a glacial–interglacial doubling of methane concentrations<sup>3–5</sup>. The processes driving the observed fluctuations remain uncertain but can be constrained using methane isotopic information from ice cores<sup>6,7</sup>. Here we present an ice core record of carbon isotopic ratios in methane over the entire last glacial–interglacial transition. Our data show that the carbon in atmospheric methane was isotopically much heavier in cold climate periods. With the help of a box model constrained by the present data and previously published results<sup>6,8</sup>, we are able to estimate the magnitude of past individual methane emission sources and the atmospheric lifetime of methane. We find that methane emissions due to biomass burning were about 45 Tg methane per year, and that these remained roughly constant throughout the glacial termination. The atmospheric lifetime of methane is reduced during cold climate periods. We also show that boreal wetlands are an important source of methane during warm events, but their methane emissions are essentially shut down during cold climate conditions.

The atmospheric concentration of CH<sub>4</sub>, the second most important anthropogenic greenhouse gas, is determined by a balance between natural and anthropogenic CH<sub>4</sub> sources and sinks that is still debated. Photochemically induced oxidation in the troposphere and stratosphere, and uptake by methanotrophic bacteria in aerated soils, represent the most important sinks<sup>9,10</sup>. The dominating natural CH<sub>4</sub> sources comprise tropical and boreal wetlands, ruminants, and biomass burning<sup>10,11</sup>. These sources all differ in their carbon and hydrogen isotopic signature. In addition, a release of CH<sub>4</sub> from marine gas hydrates<sup>12,13</sup> and emissions from plants under aerobic conditions are currently debated<sup>14,15</sup>. Most probably all those sources and sinks were subject to palaeoclimatic changes, as reflected by CH<sub>4</sub> being as low as 360 parts per billion (10<sup>9</sup>) by volume (p.p.b.v.) during the Last Glacial Maximum (LGM), compared with up to 725 p.p.b.v. in the preindustrial Holocene epoch<sup>3,16,17</sup>. Throughout the glacial period and during the last transition, CH<sub>4</sub> changed by up to 200 p.p.b.v. (refs 3, 18) in parallel with rapid climate changes. Using the interhemispheric CH<sub>4</sub> gradient in ice cores, an increase of high-latitude CH<sub>4</sub> sources in the Northern Hemisphere was derived for warm periods<sup>3,17</sup>. However, a more detailed quantitative source attribution is still missing.

Such quantitative constraint on the sources can be derived from methane isotopic measurements on ice cores<sup>6,7</sup>, making use of the different isotopic signatures of the CH<sub>4</sub> sources and the different isotopic fractionation factors for the individual removal processes (Supplementary Table 1). In Fig. 1 typical isotopic signatures for

different CH<sub>4</sub> sources are summarized, spanning a wide range of  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta\text{D}(\text{CH}_4)$ . This shows that  $\delta^{13}\text{C}_{\text{CH}_4}$  strongly constrains the amount of CH<sub>4</sub> released by biomass burning, because pyrogenic CH<sub>4</sub> is the only natural source strongly enriched in <sup>13</sup>C. The fractionation caused by the sinks is illustrated by the offset of the isotopic signature in atmospheric CH<sub>4</sub> and the calculated emission averages. This fractionation is very pronounced (~200‰) for  $\delta\text{D}(\text{CH}_4)$  but rather small (5–7‰) for  $\delta^{13}\text{C}_{\text{CH}_4}$ .

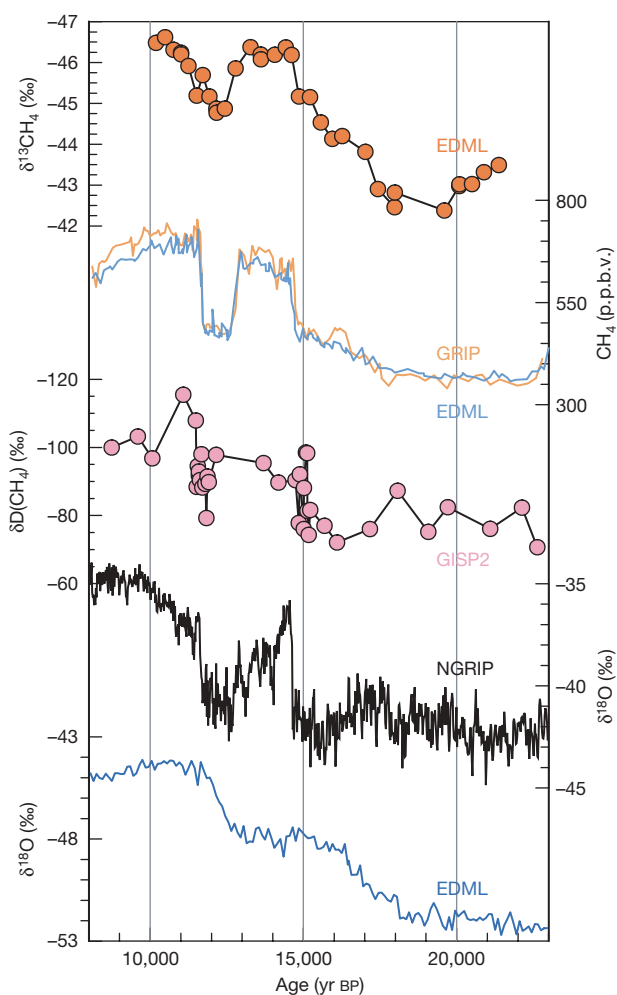


**Figure 1 | Typical carbon and hydrogen isotopic signatures of different CH<sub>4</sub> sources used in the Monte Carlo model.** Data are from refs 10 and 11 and references therein. Mainly anthropogenic sources are indicated by open circles, mainly natural sources by dark grey dots. The error bars indicate the spread of reported values<sup>10</sup>. No  $\delta\text{D}$  values for plant emissions are available so far. We used a value of  $-290\text{‰}$ , which does not influence our model outcome. Open stars indicate the modelled average atmospheric  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta\text{D}(\text{CH}_4)$  for the 1990s, preboreal Holocene (PB), Younger Dryas (YD), Bølling/Allerød (BA) and LGM. Filled stars represent best-guess model estimates for average  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta\text{D}(\text{CH}_4)$  emitted, where we limited atmospheric lifetimes to values larger than 5 yr. The dashed line represents a linear fit through these isotopic emission averages.  $\delta\text{D} = [(D/H)_{\text{sample}} / (D/H)_{\text{standard}}] - 1$  in ‰, where standard is standard mean ocean water (SMOW);  $\delta^{13}\text{C} = [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}}] - 1$  in ‰, where standard is VPDB

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Using high-precision gas chromatography isotope ratio mass spectrometry (see Supplementary Information) we have been able to derive a high-resolution  $\delta^{13}\text{CH}_4$  ice-core record over the last glacial–interglacial transition. We carried out carbon isotopic analyses on 34 samples from the EPICA (European Project for Ice Coring in Antarctica) ice core from Dronning Maud Land (EDML)<sup>8</sup>. With its present accumulation rate of 6.4 cm water equivalent per year and an age distribution (width at half maximum) in the air bubbles of 60 yr, this core is especially suited to derive higher-resolution records over the last glacial cycle.

In Fig. 2 our  $\delta^{13}\text{CH}_4$  record is plotted together with the  $\text{CH}_4$  concentrations from the EDML and the Greenland GRIP ice core<sup>3,8</sup>. Clearly, the most conspicuous features of our  $\delta^{13}\text{CH}_4$  data are the high isotopic values of around  $-42.8\text{‰}$  during the LGM followed by a  $3.5\text{‰}$  decrease to about  $-46.3\text{‰}$  during the preboreal Holocene. The preboreal value is about  $0.8\text{‰}$  more enriched than values from the Law Dome ice core (Antarctica)<sup>19</sup> for the time interval 1–2 kyr before present (BP) when  $\text{CH}_4$  was about 40 p.p.b.v. lower<sup>17</sup>. At the same time the interhemispheric  $\text{CH}_4$  gradient<sup>17</sup> and, thus, the boreal methane source strength was comparable. This implies a relatively higher contribution of isotopically light boreal  $\text{CH}_4$  emissions to the



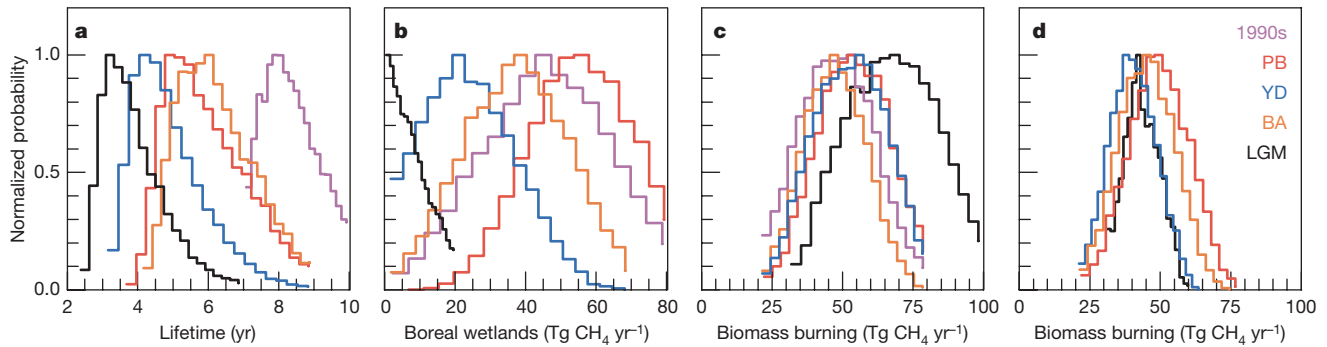
**Figure 2 | Glacial/interglacial changes in methane and climate.** Carbon isotopic signature of methane (scale reversed) in the EDML ice core together with Greenland (GRIP) and EDML methane concentrations<sup>3,8</sup>,  $\delta\text{D}(\text{CH}_4)$  in the GISP2 ice core<sup>6</sup> (scale reversed) and the temperature proxy  $\delta^{18}\text{O}$  from EDML<sup>5</sup> and NGRIP<sup>1</sup>. All data sets are given on the GICC05 age scale after  $\text{CH}_4$  synchronization<sup>8</sup>, except for GISP2  $\delta\text{D}(\text{CH}_4)$  data given on their individual methane synchronized age scale<sup>6</sup>. Values of  $\delta^{13}\text{CH}_4$  were corrected for gravitational enrichment in the firn column (see Supplementary Information) and are referenced against VPDB.

total  $\text{CH}_4$  budget in the late preindustrial Holocene compared with the preboreal Holocene. Alternatively, the lower  $\delta^{13}\text{CH}_4$  values could be affected by increased rice cultivation and/or livestock in the late Holocene. Whether a significant anthropogenic influence on  $\text{CH}_4$  had already started by 5000 yr BP as recently hypothesized<sup>20</sup> cannot be answered at this point.

Our  $\delta^{13}\text{CH}_4$  record shows also significant variations in parallel with the rapid  $\text{CH}_4$  changes during the Bølling/Allerød–Younger Dryas oscillation, with  $\delta^{13}\text{CH}_4$  values during the Bølling/Allerød similar to the preboreal Holocene (about  $-46.3\text{‰}$ ) but with slightly lower  $\text{CH}_4$  concentrations. During the Younger Dryas,  $\delta^{13}\text{CH}_4$  increased to around  $-45\text{‰}$ . Our data do not support  $\delta^{13}\text{CH}_4$  values during the Younger Dryas/preboreal transition measured on outcropping ice on the west Greenland margin<sup>7</sup>, which generally show isotopically lighter  $\delta^{13}\text{CH}_4$  values before than after the end of the Younger Dryas. In view of the much higher scatter of those data and the potential of isotopic artefacts occurring in this warm outcropping ice, we think that our high-precision ice-core data reflect more closely the isotopic changes in atmospheric methane.

In principle, changes in the source as well as in the fractionation of the sinks may contribute to the observed changes. The latter effect is small because a global glacial–interglacial temperature increase of  $5^\circ\text{C}$  would decrease the carbon isotope fractionation by only  $0.2\text{--}0.3\text{‰}$ <sup>21–23</sup> and also changes in lifetime have a negligible effect on  $\delta^{13}\text{CH}_4$ . Accordingly, the  $\delta^{13}\text{CH}_4$  values indicate mainly a shift to isotopically heavier sources during cold climate periods. Thus, either an isotopically enriched  $\text{CH}_4$  source (such as biomass burning) increased, or a depleted source (such as wetlands) decreased. Considering the 50% reduction of atmospheric  $\text{CH}_4$  concentrations and the lack of an interhemispheric gradient in the LGM, a reduction of boreal wetland emissions is more likely. To constrain the emission by individual sources, we used a simple model of the  $\text{CH}_4$  cycle with two tropospheric and two stratospheric boxes driven by prescribed emission fluxes for time intervals of relatively constant  $\text{CH}_4$ : the preboreal Holocene, Younger Dryas, Bølling/Allerød and LGM (see Supplementary Information). The model has been validated for recent conditions and reflects  $\text{CH}_4$  observations very well. For the last deglaciation our  $\delta^{13}\text{CH}_4$  data from EDML, together with  $\delta\text{D}(\text{CH}_4)$  data from Greenland<sup>6</sup> and  $\text{CH}_4$  concentrations from both polar regions<sup>3,8,16</sup>, provide four constraints for the model. However, with six natural sources and three sink processes, the solution of the model is still underdetermined. To find possible solutions we used a Monte Carlo approach (see Supplementary Information). For many of the sources, the resulting probability distributions are not discriminating, owing to a considerable overlap in the isotopic signatures. However, robust quantitative constraints can be derived for the atmospheric lifetime, biomass burning and boreal wetland emissions.

In our initial estimate, which is constrained only by ice-core observations (see Supplementary Information), the atmospheric lifetime decreased from the recent value of a little more than 8 yr to around 5.6 yr in the preboreal Holocene and Bølling/Allerød, in good agreement with estimates of preindustrial runs using a three-dimensional model of chemistry and transport<sup>24</sup>. In the Younger Dryas our most likely result indicates a strong lifetime decrease to 4.4 yr and to 3.7 yr in the LGM (Fig. 3a). Although a lifetime decrease is expected from the much lower atmospheric  $\text{CH}_4$  concentration and reduced emissions of volatile organic carbon species during the LGM<sup>25,26</sup>, this decrease of more than 50% relative to present is much stronger than predicted by current estimates from a three-dimensional chemistry model<sup>26</sup>. However, as also shown in Fig. 3, lifetimes similar to those model estimates also fulfil our data constraints, but are less likely. Such longer lifetimes require a reduction in tropical wetland emissions to explain the lower  $\text{CH}_4$  concentrations during the LGM. In summary, data as well as models indicate a shorter  $\text{CH}_4$  lifetime during past climate periods in the range of 3–7 yr.



**Figure 3 | Methane box model results.** Normalized probability functions (NPF) for (a) atmospheric lifetime, (b) boreal wetland and (c) biomass burning emissions for the 1990s (pink), preboreal Holocene (PB, red), Younger Dryas (YD, blue), Bølling/Allerød (BA, orange) and the LGM (black) as derived in our data-constrained Monte Carlo box model. d, The

The higher atmospheric  $\delta\text{CH}_4$  together with the lack of an inter-hemispheric  $\text{CH}_4$  gradient requires the boreal wetland source in our model to be essentially shut down during the LGM, in line with the extreme cold and vastly expanded continental ice sheets in the high-latitude Northern Hemisphere. Part of the carbon isotope variation observed over the transition may also stem from a shift in the wetland substrate from C4 to C3 plants, following different photosynthetic pathways. However, such a shift cannot explain the size of the observed  $\delta^{13}\text{CH}_4$  change or the changes in the interhemispheric gradient. A reduction of boreal wetlands connected to a reduced inter-hemispheric  $\text{CH}_4$  gradient and more enriched  $\delta^{13}\text{CH}_4$  is also supported for the Younger Dryas. In contrast, the  $\delta^{13}\text{CH}_4$  values derived from outcropping ice on the west Greenland margin<sup>7</sup> show isotopically lighter  $\delta^{13}\text{CH}_4$  values during the Younger Dryas, which are difficult to reconcile with the interhemispheric gradient indicating a decrease in boreal  $\text{CH}_4$  emissions.

Furthermore, quantitative constraints are derived from our  $\delta^{13}\text{CH}_4$  data for pyrogenic  $\text{CH}_4$  emissions. In our initial estimate (allowing for short atmospheric lifetimes) our model suggests somewhat higher biomass burning emissions during the LGM, where significant changes in vegetation cover and aridity occurred<sup>27,28</sup>. When we additionally constrain atmospheric lifetimes in Fig. 3d to longer than 5 yr in line with chemistry models, our best-guess estimate for biomass burning emissions remains close to about  $45 \text{ Tg CH}_4 \text{ yr}^{-1}$  throughout the transition, with slightly lower biomass burning during cold periods. Evidence for temporally constant biomass burning emissions is also provided by global vegetation modelling<sup>29</sup>, but the modelled biomass burning  $\text{CH}_4$  emission is 50% lower than our Monte Carlo estimate.

Secondary trends in  $\delta^{13}\text{CH}_4$  occurred during the LGM and preboreal Holocene. For instance  $\delta^{13}\text{CH}_4$  decreased slowly during the preboreal Holocene, when temperatures in Greenland and the  $\text{CH}_4$  concentration gradient slightly increased. This may be attributed to expanding boreal sources, for example related to increased thermokarst emissions at that time<sup>30</sup>. During the late glacial (22,000–20,000 yr BP),  $\delta^{13}\text{CH}_4$  slowly increased by about 1‰ while  $\text{CH}_4$  remained constant. A change in the carbon isotopic signature of the biomass fuelling wildfires by 3‰, caused by of a shift from C3- to C4-dominated grasslands, could largely explain this secondary trend in  $\delta^{13}\text{CH}_4$  despite constant biomass burning emissions. Alternatively, it may represent a slow reduction of wetland emissions compensating a synchronous increase in biomass burning emission.

The result of our steady-state modelling is indicated by the average signatures of  $\text{CH}_4$  emissions for past conditions in Fig. 1. These best-guess average emissions lie on a line roughly through the wetland isotopic signature, illustrating the changing influence of boreal wetland emissions on the isotopic  $\text{CH}_4$  budget. This clearly shows that a  $\text{CH}_4$  contribution from deuterium-enriched marine gas hydrates is

not supported by the observed isotope changes. However, quantification of a short  $\text{CH}_4$  outburst from marine hydrates will require more high-resolution isotope data around rapid climate warmings together with time-resolved isotope modelling of the atmospheric  $\text{CH}_4$  cycle and diffusion effects in the firn column. In summary, our new carbon isotopic constraint is able to determine the change in average  $\text{CH}_4$  emissions from boreal wetlands and biomass burning very well, showing that the latter source was surprisingly stable over a wide range of climate conditions. This provides an important test for vegetation models and together with revised atmospheric chemistry models will improve our understanding of the oxidative capacity of the atmosphere in the past.

## METHODS

We performed  $\delta^{13}\text{CH}_4$  measurements on 150–200 g of ice using a purge and trap extraction coupled to a gas chromatography isotope ratio mass spectrometer. We separated  $\text{CH}_4$  from other gases using gas chromatography and quantified isotopic ratios on  $\text{CO}_2$  after quantitative combustion of  $\text{CH}_4$ . Absolute standardization is achieved in every run using (i) a pure  $\text{CO}_2$  standard (ii) a pure  $\text{CH}_4$  standard admitted to the gas chromatography helium stream and (iii) 10 ml (STP) of a synthetic air standard admitted into the extraction vessel. All  $\delta^{13}\text{CH}_4$  values are referenced against Vienna PeeDee belemnite (VPDB) and corrected for gravitational enrichment. Replicate samples from the EDML ice core have been measured on five depth intervals showing a mean standard deviation of  $\pm 0.09\text{‰}$  with somewhat larger uncertainties for glacial samples with low  $\text{CH}_4$  concentration. This is also in line with the reproducibility of the air standards. In summary, we estimate the reproducibility of our measurements to be better than 0.15‰.

Potential source emissions were determined in steady state using a box model of the atmospheric  $\text{CH}_4$  cycle. The atmosphere is divided into northern and southern tropospheric and stratospheric boxes with prescribed air mass exchange. Methane emissions into the northern and southern troposphere are prescribed with fixed isotopic signatures (refs 10, 11 and references therein; Supplementary Table 1). The model takes into account oxidation in the troposphere and stratosphere and uptake by aerated soils<sup>10</sup>. To constrain  $\text{CH}_4$  emissions in the past the model was run in a Monte Carlo mode, where emissions of each individual source and the lifetime were randomly picked within reasonable limits and compared with the data constraints.

For more details on the analyses and model used, see Supplementary Information.

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**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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